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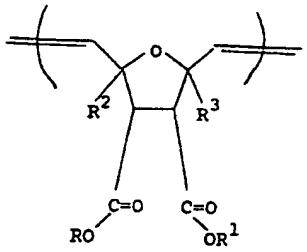
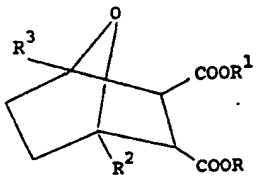
(54) Process for polymerizing oxanorbornenes and polymers obtainable by the process

(57) A process for the preparation of a polymer containing units of formula (I)



(I)

, wherein R represents a hydrogen atom or alkyl, cycloalkyl or aryl (which group may be substituted), R^1 is alkyl, aryl or cycloalkyl (which group may be substituted) and R^2 and R^3 are hydrogen or alkyl, comprise reacting a monomeric starting material comprising a compound of formula II.



(II)

, where R, R^1, R^2 and R^3 are as defined above, in the presence of an aqueous catalyst system comprising a compound of a metal of Group VIII (e.g. Ru Cl_3).

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PROCESS FOR POLYMERIZING OXANORBORNENES AND POLYMERS OBTAINABLE BY THE PROCESS

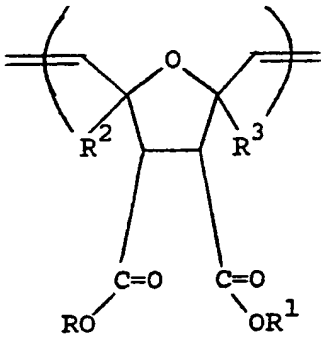
This invention relates to a process for the polymerization of certain derivatives of oxanorbornene and to novel polymers obtainable by the process.

The metathesis polymerization of mono - and diester derivatives of bicyclo [2.2.1] hept - 2 - ene (norbornene) is described in US 3557062. The polymerization, to give polymers with low glass transition temperatures, useful in the preparation of vulcanizable elastomeric compositions, proceeds under substantially anhydrous conditions in the presence of the metal catalyst such as ruthenium chloride and in the presence of the esterifying alcohol. When attempting to polymerize the diesters, it was found that the steric configuration of the starting material determined the ability to polymerize. Thus bicyclo[2.2.1]hept-2-ene-dicarboxylic - 5, 6 acid and its esters, when obtained from the product of the reaction of maleic anhydride with cyclopentadiene, was in the "endo" - cis steric configuration and could not be polymerised unless first converted to the exo-cis form.

Metathesis polymerization of oxanorbornene derivatives using an aqueous catalyst system has been described by Novak and Grubbs, J.Am. Chem. Soc., 110, (1988), 7542 - 7543. Those authors describe the polymerization of the 2,3-dimethoxymethyl derivative of 7-oxabicyclo [2.2.1] hept-5-ene (oxanorbornene). Although such oxanorbornene ring systems can be prepared by Diels - Alder synthesis, the introduction of the required functional groups at the 2, 3 positions requires additional preparative steps.

It has surprisingly been found, in accordance with the present invention, that 7-oxanobornene compounds having a carboxyl substituent at each of the 2 and 3 positions, at least one of which has been esterified, can be readily polymerized in an aqueous catalyst system without the difficulties encountered as described in US 3557062.

According to the present invention there is provided a process for the preparation of a polymer containing units of the general formula I



(I)

wherein R represents a hydrogen atom or an alkyl, cycloalkyl or aryl group (which group may be substituted), R^1 is an alkyl, aryl or cycloalkyl group (which group may be substituted) and R^2 and R^3, which may be the same or different, represent a hydrogen atom or an alkyl group, comprising reacting

compounds, for example a mixture of mono - and di-esters.

The catalyst system preferably comprises a compound of a metal selected from ruthenium, osmium and rhodium, more preferably ruthenium. The compound may be inorganic, for example a chloride, or organic, for example a cyclooctadiene adduct, a p-toluene sulphonate or a trifluoromethyl sulphonate. Mixtures of metal compounds may be employed. The amount of metal compound used is suitably within the range of from 10^{-5} to 10^{-1} moles metal compound per mole of monomer.

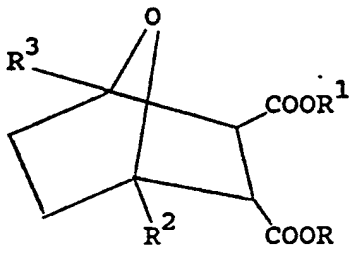
The catalyst system further comprises water. Suitably the amount of water initially present is from 10 mole % to 1000 mole % based on the compound of formula (II).

If the ester of formula II has been directly prepared by esterification of the corresponding anhydride, the polymerization may be effected by adding the required quantity of additional water to that already produced in the esterified reaction mixture, with isolation of the ester being unnecessary.

The polymerization is suitably carried out under comparatively mild conditions, for example at temperatures within the range of from 30 to 120°C, suitably at atmospheric pressure. The time of polymerization may vary widely dependent on the desired properties of the product polymer. Suitable reaction times range from 6 minutes to 10 hours.

The resulting polymeric product may be isolated from the reaction mixture by any suitable means such as filtration or various well known extraction procedures.

a monomeric starting material comprising a compound of formula II



(II)

where R, R^1, R^2 and R^3 are as defined above, in the presence of an aqueous catalyst system comprising a compound of a metal of Group VIII. Metals of Group VIII are as defined in the Periodic Table of the Elements, Handbook of Chemistry and Physics, 64th Edition, 1983/84.

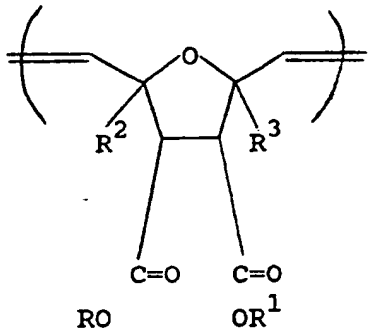
Preferably R^2 and R^3 in the compound of formula I represent hydrogen atoms. Preferably R represents a hydrogen atom or an alkyl group and R^1 represents an alkyl group. A preferred compound is one in which R^2 and R^3 represent hydrogen atoms and R and R^1 are methyl.

Compounds of formula II can be readily prepared from the corresponding 2,3 - anhydride by esterification with the desired esterifying alcohol in an amount suitable to give the monoester or diester as required. The starting anhydride where R^1 and R^2 are hydrogen is commercially available, ie. endo 7- oxabicyclo (2.2.1) hept-5-en-2,3-dicarboxylic acid anhydride. Alternatively such anhydrides can be readily prepared using the well known Diels - Alder condensation of maleic anhydride and furan.

The monomeric starting material may consist of a single compound of formula II or a mixture of such

While the water present in the system may serve as the sole reaction medium, other inert solvents and/or liquid media may be present such as ethers and/or alcohols.

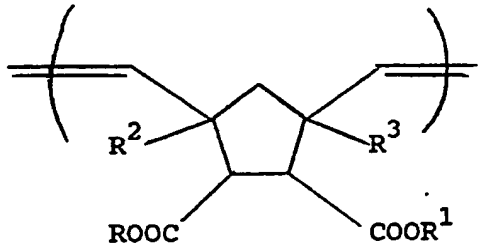
The product polymers containing units of formula I are novel materials. Therefore, according to a further aspect of the present invention there is provided a polymer containing units of the general formula I



(I)

,where R, R^1, R^2 and R^3 are as previously defined.

The polymer may be a homopolymer or a random or block copolymer. If desired, the polymer prepared as described above, may be further reacted with an additional monomer, such as a dicyclopentadiene monomer, to yield a copolymer, suitably as a block copolymer. A preferred additional monomer is a norbornene derivative, preferably analogous to the oxanorbornene monomer of formula I, thus yielding a copolyner containing units of formula I together with units of formula III



(III)

,where R, R^1, R^2 and R^3 are as previously defined.

It will be readily appreciated that the product homo- and copolymers have highly reactive functional groups. Dependent on the functional groups, they may be further derivatized and find application for example in the field of detergents and lubricant additives, as well as in the field of elastomers, as suggested in US 3557062.

The invention will now be further described with reference to the following examples.

Example 1

Endo 7 - oxabicyclo (2.2.1.) hept-5-en-2,3-dicarboxylic acid anhydride (10 g) was esterified with methanol (80 ml) in the presence of p-toluene sulphonic acid (1 mole). The reaction was carried out at a temperature of 65°C for a period of 5 hours and the product diester recovered by overhead distillation of 90% of the remaining methanol from the diester.

7-oxa-5-norbornene-2,3-dicarboxylic acid dimethyl ester prepared as just described and containing residual methanol (6g) was mixed with water (10g) and ruthenium chloride (0.5 mmol). The reaction mixture was heated to 60°C and the reaction allowed to proceed for 1 hour. Polymeric product (3g) was isolated by filtration. The product was identified as polyoxanorbornene dimethyl ester, some

10% of the ester groups having been hydrolysed to carboxylic acid groups. Identification was effected by 13C nmr analysis.

Example 2 (Comparative)

The starting material of Example 1, ie. endo 7-oxabicyclo(2.2.1)hept-5-en-2,3-dicarboxylic acid anhydride (6g) was directly polymerized without initial esterification in the presence of water (10g) and ruthenium chloride (0.5 mmol). The reaction was carried out for 1 hour at 60°C followed by 2 hours at 90°C. No polymer formation was observed.

Example 3 (Comparative)

5-norbornene-2,3-dicarboxylic acid dimethyl ester (6g), obtained by esterification of the corresponding anhydride by the method described in Example 1, was mixed with water (10g) and ruthenium chloride (0.5 mmol). Reaction was carried out for 2 hours at 60°C followed by 2 hours at 90°C. No polymer formation was observed.

Example 4

The polymer obtained in Example 1 (and still containing catalyst) (1g) was added to a mixture of 5 - norbornene-2,3-dicarboxylic acid dimethyl ester (10g) and water (10 ml). The mixture was allowed to react for 5 hours at 80°C. A polymer product was isolated (3g), which was shown by nmr analysis to consist of 37% polyoxanorbornene dicarboxylic acid dimethyl ester and 63% by weight of polynorbornene dicarboxylic acid dimethyl ester.

It will be readily appreciated from the foregoing examples that 7-oxa-5-norbornene -2,3-dicarboxylic acid dimethyl ester can readily be

polymerized under comparatively mild conditions with an aqueous catalyst system (Example 1), while the corresponding anhydride cannot be polymerized, even under more severe conditions (Comparative Example 2). Also, suprisingly, the chemically analogous norbornene ester will not polymerize (Comparative Example 3), even under more severe conditions than those for the oxanorbornene ester.

Example 4 demonstrates that once polymer has formed it is possible to copolymerize with the norbornene derivative to obtain a copolymer including both cyclopentane and furan ring structures.

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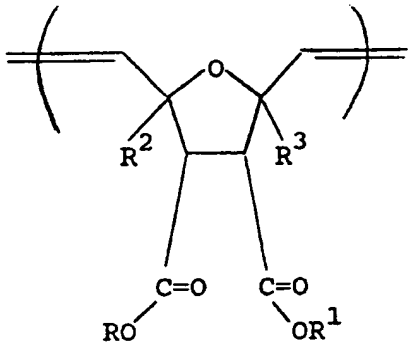
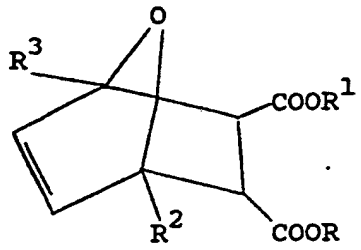
CLAIMS

1. A process for the preparation of a polymer containing units of the general formula I



(I)

,wherein R represents a hydrogen atom or an alkyl, cycloalkyl or aryl group (which group may be substituted), R^1 is an alkyl, aryl or cycloalkyl group (which group may be substituted) and R^2 and R^3, which may be the same or different, represent a hydrogen atom or an alkyl group, comprising reacting a monomeric starting material comprising a compound of formula II



(II)

,where R, R^1, R^2 and R^3 are as defined above, in the presence of an aqueous catalyst system comprising a compound of a metal of Group VIII.

2. A process according to claim 1 wherein R^2 and R^3 in formulae I and II represent hydrogen atoms.

3. A process according to claim 1 or 2 wherein R and R^1 are methyl.

4. A process according to any one of the preceding claims wherein the compound of formula II has been prepared by esterification of the corresponding anhydride.

5. A process according to any one of the preceding claims wherein the metal compound is a compound of ruthenium, osmium or rhodium.

6. A process according to claim 5 wherein the metal compound is ruthenium chloride.

7. A process according to any one of the preceding claims wherein the metal compound is present in an amount within the range of from 10^{-5} to 10^{-1} moles metal compound per mole of monomer.

8. A process according to any one of the preceding claims wherein water is present initially in an amount of from 10 mole % to 1000 mole % based on the compound of formula II.

9. A process according to any one of the preceding claims wherein the polymerization has been

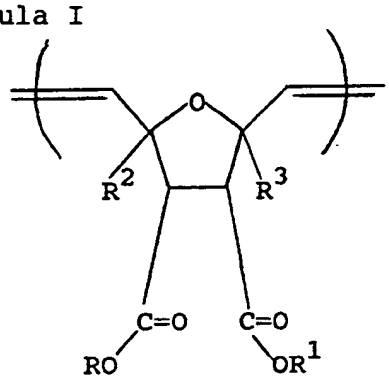
carried out at a temperature of from 30 to 120°C.

10. A process according to any one of the preceding claim wherein the polymer product is further reacted with a further monomer selected from dicyclopentadienes and norbornenes.

11. A process for polymerizing a monomer of general formula II substantially as described herein with reference to Example 1 or 4.

12. A polymeric product when obtained by the process of any one of the preceding claims.

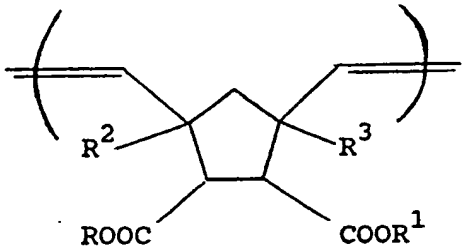
13. A polymer containing units of the general formula I



(I)

,where R, R^1, R^2 and R^3 are as defined in claim 1.

14. A polymer according to claim 13 which further contains units of formula III



(III)

where R, R^1, R^2 and R^3 are as defined in claim 1.

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